

Title: Method for pretreating a surface of a non-conducting material to be plated

**Technical Field**

The present invention relates to a method for pretreating a surface of a non-conducting material to be plated by way of precipitation of metal in the presence of a catalytic metal, and optionally to be subjected to a subsequent electrolytic plating or another type of surface treatment. By the method, the surface is activated by a catalytic metal, such as palladium.

When the surface is activated in such a manner where the activating metal for instance is a metallic palladium, viz. oxidation step 0, the palladium acts as an efficient catalyst for the precipitation of metal, such as copper, cobalt, silver, tin, gold or nickel. In this manner it is possible to provide an electrically conducting metal layer on the surface of a non-conducting material, on which, if desired, an additional layer of metal can be applied from an aqueous or an organic electrolyte by way of a conventional coating process, such as by way of an electrolytic plating process. Non-limiting examples of metals capable of being applied after the first precipitation of metal are for instance metal layers of Ni, Cu, Ag, Au, Sn and In.

**Background Art**

It is well-known that non-conducting materials, such as ceramics (a technical nomenclature for British "ceramics", viz. ceramics), glass and plastics, can be plated when the surface is made electrically conducting. This can be carried out by way of a precipitation of metal, such as copper or nickel. The precipitation of metal can for instance be an autocatalytic precipitation of metal, which is also called a chemical plating, but such a precipitation of metal requires a previous treatment of the surface in form of an etching and an activation for instance by means of palladium.

The etching of the non-conducting material results in formation of small pores in the

surface, and the metal can be anchored in said small pores. The etching can be carried out by means of an oxidant. After the etching procedure, both the excess oxidant and the reaction product resulting from the oxidizing process are removed, said substances being undesirable at the subsequent plating process.

- 5 Examples of oxidants for the etching are chromic sulphuric acid ( $\text{CrO}_3$  + sulphuric acid) and potassium permanganate ( $\text{KMnO}_4$ ). The use of the latter substance has the effect that the resulting reaction product is manganese dioxide (pyrolusite;  $\text{MnO}_2$ ). In order to ensure an efficient removal of the manganese dioxide, a sulphuric acid solution is usually used.
- 10 After the etching, the surface is activated by means of colloidal palladium ( $\text{Pd}(0)$  surrounded by  $\text{Sn}^{+++}$ ). The tin ions are then chemically removed through a complex formation with the result that the metallic palladium is left in the small pores of the surface where said tin ions catalyze a subsequent chemical plating, in particular together with nickel or copper.
- 15 The chemical plating catalyzed in this manner results in a metal layer covering the entire treated surface, and it is now possible to carry out any chemical or electrolytic treatment or any other surface treatment which can be conventionally used on conducting materials.

The above known method is suitable for plating some polymeric materials, especially  
20 such materials including several phases, where one of the phases can be etched away in the surface, such as for instance the butadiene phase in ABS plastics. Other types of plastics are also suitable, such as polypropylene, polyphenylene oxide, nylon (6.6) and Teflon®. However, the selection of suitable types of plastics is limited. Many intended utilizations are already presented to many requirements with respect to the  
25 plastic materials used, and it is desirable to be able to plate a wider range than previously of types of plastics without giving up other vital properties of the type of plas-

tics in question.

Even the plastics capable of being plated by means of the method described are encumbered with the further draw-back that a very strong oxidative etching is necessary in order to achieve a sufficient fixation of the palladium ions, which in turn is necessary for the fixation of the chemical plating layer. The oxidative etching of the polymer in question causes in connection with multi-phased, such as two-phased polymers, often a varying etching speed for the individual phases. As a result, small cavities or pores are formed in which it is possible to mechanically lock (interlock) a subsequent chemically precipitated metal layer. The oxidative etching can optionally be supplemented with an advance mechanical raising (making rough) in order to achieve an improved physical adhesion.

US-PS No. 4 999 251 (Foust et al.) discloses a method of pretreating polyetherimide (PEI) prior to a conventional activation by means of a solution of palladium chloride in hydrochloric acid. After treatment with a degreaser, the PEI-surface is initially treated with concentrated sulphuric acid. Then follows a treatment with an aqueous base to pH 14 or higher. After treatment with permanganate, the resulting manganese dioxide is then removed by means of hydroxylamine hydrochloride, which irritates the skin and is difficult to handle. According to the publication, the method can be used for pretreatment and activation of PEI for a subsequent autocatalytic plating. However, the method is complicated and involves the use of heavily etching and irritating chemicals, and is not believed to have found industrial propagation.

US-PS No. 5 693 209 (Bressel et al.) discloses a process for metallizing circuit boards with a non-conducting surface. After the oxidation of the surface by means of permanganate, the deposited manganese dioxide is allowed to remain on the surface after a washing away of the excess permanganate. Then the surface is treated with pyrrole monomer and pyrrole oligomer in a weak acid with the result that an electrically conducting insoluble polymer is deposited which can subsequently be subjected

to a direct plating. The process is suitable on epoxy resin boards, but does not present a wide-spectrum applicability on various types of plastics. In addition, the metallization is carried out at a low speed involving heterogeneous metal coatings, and the process is not suitable for plating large surfaces requiring a base layer presenting a good electric conductivity. The latter requirement cannot be met by the electrically conducting polymer.

US-PS No. 5 078 889 discloses a specially-treated electrolytic manganese dioxide of the  $\gamma$ -type for a selective removal of contaminants from drinking water. It is inter alia stated that the described manganese dioxide can remove small amounts of heavy metals from the drinking water by way of adsorption.

EP 0414 097 describes a method whereby a conducting metal layer is formed by a reduction of metal compounds so as thereby to establish an electric conductivity on the surface of a polymer. As a result, it is possible to apply further coatings by way of electrolysis. After a pretreatment, an adhesive is applied onto the surface. This adhesive can be selected among metal oxide, metal hydroxide or metal carbonate, and can according to an embodiment be manganese dioxide resulting from reduction of permanganate. Subsequently, a metal compound is adsorbed, said metal compound being selected among almost all such metals capable of being reduced by means of a suitable reducing agent. Gold, silver, cobalt, nickel, iron and other metals have been suggested. Subsequently, a treatment is carried out by means of a strong reducing agent so as to form a metal layer which together with manganese dioxide must be capable of forming an electrically conducting layer without the use of autocatalytic baths. This step is difficult and can easily result in the entire process being unsuccessful. The process can presumably be used for plating circuit boards, but it is hardly useful for plating large areas.

### **Brief Description of the Invention**

It turned out that a change of the pretreating method renders it possible to achieve an

improved and widely applicable pretreatment of the surface of a non-conducting material to be plated.

Thus the present invention relates to a method for pretreating a surface of a non-conducting material to be plated by way of precipitation of metal in the presence  
5 of a catalytic metal, and optionally to be subjected to a subsequent electrolytic plating or another type of surface treatment.

The method is characterised by

- a) depositing an adsorbing metal oxide on the surface,
  - b) treating the surface with a solution of transition metal ions, and subsequently
  - 10 c) treating the surface with a solution of catalytic metal ions,
- where the transition metal ions used in step (b) are selected among such ions which can reduce catalytic metal ions into catalytic metal.

According to an embodiment of the method according to the invention the depositing of the adsorbing metal oxide in form of manganese dioxide can be carried out by  
15 oxidizing the surface in step (a) by means of a permanganate compound while forming manganese dioxide, and by washing away the remaining permanganate compound after the oxidation without removing the formed manganese dioxide deposited in form of a layer or in form of small clusters on the surface.

Step (b) can according to an embodiment be carried out by treating the surface with  
20 an aqueous solution of  $\text{Sn}^{++}$  ions.

The catalytic metal ions used in step (c) are ions of a metal catalyzing the autocatalytic precipitation, such as a metal from the platinum group, preferably  $\text{Pd}^{++}$ ,  $\text{Rh}^{++}$  or  $\text{Pt}^{++}$ .

The method according to the invention renders it possible to plate non-conducting

materials and matrixes where a conventional electrolytic or autocatalytic treatment is unsuitable or can only be carried out with difficulties. In addition, it allows other processes requiring an electrically conducting surface, such as electrostatic powder lacquering.

- 5 The non-conducting material can also be a non-conducting matrix including reinforcing fibres and/or fillers based on organic and/or inorganic matter. When such included materials are electrically conducting per se, the pretreatment by the method according to the invention can activate the surface so as to obtain a uniform precipitation of metal.
- 10 The extent of applicability of the invention appears from the following detailed description. It should, however, be understood that the detailed description and the specific examples are merely included to illustrate the preferred embodiments, and that various alterations and modifications within the scope of protection will be obvious to persons skilled in the art on the basis of the detailed description.

## 15 Detailed Description of the Invention

The method according to the invention is based on the recognition that a deposited layer of a metal oxide on a non-conducting material, such as a plastic material, adsorbs in an efficient manner some metal ions when the metal oxide layer is immersed in a solution including such metal ions. Non-limiting examples of suitable metal  
20 oxides are manganese dioxide  $\text{MnO}_2$  and ochre ( $\text{Fe}_2\text{O}_3$ ).

It is well-known from the conventional pretreatment involving a chemical raising by means of an oxidizing permanganate compound that a layer of manganese dioxide is deposited on the treated surface during the oxidation reaction. Persons skilled in the art consider this layer of manganese dioxide undesirable during the subsequent known  
25 activating and plating process where colloidal palladium is used because experience

proves that manganese dioxide residues have a disastrous effect on the adhesion. Therefore, the layer of manganese dioxide is carefully removed together with the excess permanganate compound by the conventional pretreatment after the oxidation. As the manganese dioxide is water-insoluble, the removal must be carried out by  
5 means of an acid, such as sulphuric acid.

Unlike the conventional pretreatment, the present invention utilizes the fact that the water-insoluble manganese dioxide adheres strongly to the surface of the material in combination with the capability of adsorbing some metal ions. Instead of removing the layer of manganese dioxide by means of acid, the treated material is washed with  
10 water so as only to remove the excess permanganate compound.

This principle is used by an embodiment which has formed the initial basis for the tests which have been carried out in order to illustrate the applicability of the invention. By this embodiment, the first step (a) is a conventional etching of the surface by means of a permanganate compound, such as  $\text{KMnO}_4$ . The oxidation process re-  
15 sults in formation of manganese dioxide ( $\text{MnO}_2$ ).

Compared to the prior art, the new features of this embodiment are found in the fact that it is only necessary to remove the excess  $\text{KMnO}_4$  from the surface while  $\text{MnO}_2$  is allowed to remain in form of deposits on the surface as a thin layer or in small clusters. The latter is rendered possible by the surface being washed with water in-  
20 stead of with acid, such as sulphuric acid.

The etching by means of permanganate is assumed to result in chemical bonds between the oxidized substrate surface and the resulting manganese dioxide. Later on this binding forms the basis for the necessary adhesion of the metal to the non-conducting substrate material. Such a chemical binding does presumably also  
25 take place in connection with the permanganate etching according to the prior art, but the known binding is presumably subsequently decomposed by the treatment with

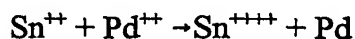
acid.

The manganese dioxide,  $\text{MnO}_2$ , and the corresponding metal oxides, such as ochre ( $\text{Fe}_2\text{O}_3$ ), present the particular property that they can adsorb a wide range of metal ions to the surface, such as  $\text{Ni}^{++}$  and  $\text{Sn}^{++}$ .

- 5 By the above embodiment it is chosen to treat the bound manganese dioxide with such a metal ion, viz.  $\text{Sn}^{++}$ , i.e. the surface is subsequently treated with a solution of a  $\text{Sn}^{++}$ -compound, such as  $\text{SnCl}_2$ , whereby  $\text{Sn}^{++}$  ions are adsorbed and thereby immobilized, viz. fixed, on the deposited  $\text{MnO}_2$ . The used solution of an  $\text{Sn}^{++}$ -compound can be neutral or weak acid, but it must not be so acid that the manganese dioxide is  
10 dissolved, which can usually be ensured by a pH-value in the range of 4 to 7.

$\text{Sn}^{++}$  is chosen as metal ion because it is a transition metal ion capable of reducing catalytic metal ions into the metallic form, such as  $\text{Pd}^{++}$  into Pd, i.e. palladium with oxidation step 0.

- The treatment with  $\text{Sn}^{++}$  is followed by a treatment with a solution of a salt of a catalytic metal, such as  $\text{PdCl}_2$  dissolved in an excess of  $\text{Cl}^-$  ions in form of  $\text{PdCl}_4^{--}$ .  
15 Palladium ions are reduced by the fixed  $\text{Sn}^{++}$  ions:



- The fixed metallic palladium is subsequently used as catalyst for the precipitation of  
20 metal.

The new pretreatment opens up the possibility of applying metal coatings, viz. plating, even onto difficult types of plastics, which cannot or which can only with great difficulty be plated by the above known methods.



By the conventional permanganate etching of plastic materials in particular, the adhesion is established by means of the activating metallic palladium during the chemical raising of the plastic surface, where micropores are etched away in the surface, said palladium being capable of being bound in said micropores by being introduced in finely dispersed, viz. colloidal, form. The chemical raising can result in a treated material presenting a dull appearance not being so aesthetic, and the method can only be used on a limited number of plastic types. By the method according to the invention the adhesion is ensured in another way, and the method according to the invention does not require the same degree of mechanical and/or chemical raising. As a result the material does not present the same dull surface characteristics, and the method opens up a possibility of treating a significantly increased number of non-conducting substrate materials.

The individual steps (a), (b) and (c) by the method according to the invention are illustrated below in general terms.

15 Step (a) deposition of metal oxide

The function of the metal oxide deposited on the surface is found in the adsorbing properties thereof. As mentioned above, such a metal oxide, viz. manganese dioxide, is deposited on the surface through a treatment of said surface by means of permanganate. However, the desired adsorbing function can also be ensured through a deposition of manganese dioxide by another chemical process or through a deposition of another metal oxide presenting the corresponding adhesive and adsorbing properties, such as ochre ( $\text{Fe}_2\text{O}_3$ ).

A non-limiting example of an alternative reaction resulting in precipitation and deposition of manganese dioxide is oxidation of an Mn(II)salt, such as manganese(II)sulphate hexahydrate or manganese dichloride:



where [Ox] can be O<sub>2</sub> or another suitable oxidant.

For precipitation and deposition of ochre, Fe<sub>2</sub>O<sub>3</sub>, a non-limiting example is correspondingly oxidation of Fe<sup>++</sup> at or on the surface where the reaction product Fe<sub>2</sub>O<sub>3</sub> is immobilized on the surface:



where [Ox] can be O<sub>2</sub> or another suitable oxidant.

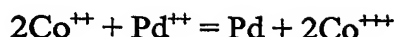
#### Step (b) treatment by means of transition metal ion

After the deposition of the adsorbing metal oxide, the material is treated with a solution including transition metal ions being adsorbed on the layer of metal oxide and thereby fixed, viz. immobilized, on the surface of the material. A preferred transition metal ion for this treatment is Sn<sup>++</sup>, and a preferred solution is a solution of SnCl<sub>2</sub>.

The solution of transition metal ions can be in any solvent in which the transition metal ions can be dissolved in a sufficiently stable form. The preferred solvent is water, but other polar solvents based on organic chemistry, such as alcohols or mixtures of water and an alcohol, can also be used.

Suitable transition metal ions are ions presenting a low oxidation step of a transition metal which forms soluble salts with several different oxidation steps, and which through reaction with a catalytic metal ion as defined below can reduce the catalytic metal ion into the free catalytic metal, viz. oxidation step 0.

A non-limiting example of usable transition metal ions in addition to the above Sn<sup>++</sup> is Co<sup>++</sup>, which can reduce Pd<sup>++</sup> according to the reaction:



Step (c) treatment with catalytic metal ions

After the treatment in step (b), the material is washed with water whereafter it is treated with a solution including ions of a catalytic metal, viz. a metal catalyzing  
5 chemical plating, especially a metal from the platinum group, such as  $\text{Pd}^{++}$  ions,  $\text{Rh}^{++}$  ions or  $\text{Pt}^{++}$  ions, such as a solution of palladium chloride ( $\text{PdCl}_2$ ). The fixed transition metal ions, such as  $\text{Sn}^{++}$  ions, reduce the catalytic metal ions into metallic form, i.e. for instance the  $\text{Pd}^{++}$  ions into metallic palladium, which is subsequently fixed to the layer of metal oxide.

- 10 The solution of catalytic metal ions can be in any solvent in which the catalytic metal ions can be dissolved in a sufficiently stable form. The preferred solvent is water, but other polar solvents based on organic chemistry, such as alcohols or mixtures of water and an alcohol, can also be used.

The method according to the invention renders it possible after a mild raising (making  
15 rough or rugged) of the surface of the material to provide the desired fixing of a catalyzing metal, such as Pd, which can catalyze a chemical plating by means of for instance copper or nickel, whereby in a manner known per se it is now possible to involve further chemical and/or electrolytic plating methods.

It turned out that the fixing obtained is so efficient that materials, such as many plastic materials, can now be plated after a pretreatment according to the invention, where  
20 previously it was not possible or only with great difficulty to plate such plastic materials.

Thus the method according to the invention turned out to be usable for pretreating  
25 polycarbonate (PC), polyphenylene oxide (PPO), polyether imide (PEI) and

acrylonitrile/butadiene/styrene-terpolymer (ABS).

The method according to the invention can be used on both thermoset and thermoplastic including plastic materials with reinforcing fibres and/or fillers, such as materials of glass, carbon, mica or titanium oxide.

- 5 In addition, the method according to the invention turned out to be usable for plating glass, ceramics, viz. ceramic material, and the like materials.

Non-limiting examples of thermoset plastics capable of being activated by the method according to the invention are polyurethane (PUR), epoxy (EP), unsaturated polyester (UP) and phenolic plastic (PF).

- 10 In addition to the above materials PC, PPO, PEI and ABS, non-limiting examples of thermoplastic capable of being activated by the method according to the invention are polyacrylamide (PAA), aliphatic or aromatic polyamide (PA), polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), polyphthalamide (PPA), polyphenylene sulphide (PPS), thermoplastic polyester (PET/PBT), liquid  
15 crystal polymer (LCP), polyetherether-ketone (PEEK), polysulphone (PSU) and polyether sulphone (PES).

- Examples of plastic materials including reinforcing substances and/or fillers capable of being pretreated and activated by the method according to the invention are glass in a matrix of polysulphone (PSU), polyether sulphone (PES) or polyacrylamide  
20 (PAA) and glass and mineral in a polyphenylene sulfide matrix (PPS). The content of reinforcing substances and/or fillers in such a type of composite materials can be relatively high. An example is polyacrylamide with 50% by weight of glass.

In the present description, the activation by means of a catalytic metal has in particular been exemplified by means of palladium. However, in principle it is possible to

use any catalytic metal originating from a solution including ions of said metal, such as a solution of a salt thereof, which is reduced by the transition metal ions fixed in the layer or clusters of metal oxide so as subsequently to be bound in the metallic form. In addition to palladium, the catalytic metal can thus be exemplified by rhodium and platinum.

The production of plastic blanks, such as by way of injection moulding, can result in material compositions or material structures deviating from the basic composition of the plastic blanks in the surface or in areas on said surface. Such areas can often complicate the adhesion to the surface of the plastic blank. Therefore, it can be necessary to carry out a mechanical or a chemical raising prior to the activation. A mechanical raising can for instance be carried out through a mild wet blowing where the additive is selected on the basis of the matrix material and the desired surface topography.

A chemical raising can for instance be in form of an etching by means of permanganate which according to the above particular embodiment is used by the method according to the invention, but which is also used by the known pretreatment described in the introduction to the description of a surface on a non-conducting material to be plated. Compared to the known pretreatment where micropores are to be formed in the surface for a fixation of palladium, the chemical raising is, however, significantly less intense by the method according to the invention.

The method according to the invention turned out to be suited for the production of plastic materials through a plating with a good electric conductivity. Thus, it is possible after a chemical plating with Cu to plate electrolytically with Cu and/or Ag, preferably with Cu first and then with Ag.

The method according to the invention can be used on any surface where it is at all possible to deposit a suitable layer or small clusters of the metal oxide. As mentioned

above, the method has turned out to be usable not only on various problematic types of plastics, but also on glass. As a result, the invention can also be used for activation of surfaces of ceramics, mineral and biological material, such as wood.

- 5 The method has been developed for activation in connection with a conventional, autocatalytic plating optionally followed by an electrolytic plating, but in principle it can be used for other purposes where a surface is to be made electrically conducting or where an insufficient conductivity is to be increased. An example is pretreatment prior to an electrostatic powder lacquering of for instance wooden furniture.

## 10 Best Embodiments of the Invention

### Example 1

- An injection moulded polycarbonate article with a complicated design is initially subjected to a mechanical raising through a wet blowing by means of glass pearls. Such a mild treatment involves a modest raising of the surface. The object of this  
15 treatment is to increase the adhesion of the plastic surface to the metal layer.

Subsequently, the plastic article is immersed for 10 minutes in an aqueous solution of 60 g/l of  $\text{KMnO}_4$  of a temperature of  $90^\circ\text{C}$ , whereafter the excess potassium permanganate was removed through rinsing in pure water.

- Then follows an immersion for 4 minutes in an aqueous solution of 100 g/l of  $\text{SnCl}_2$   
20 at room temperature and a subsequent rinsing in pure water.

Then follows an immersion for 2 minutes in an aqueous solution of 0.2 g/l of  $\text{PdCl}_2$  at room temperature and a subsequent rinsing in pure water.

The surface activated in this manner is then treated in a commercial, chemical copper-bath (Circuposit Electroless Copper 3350, Shipley Company LLC., Marlborough,

Massachusetts, USA) for 30 minutes at 45°C while forming a 2 to 3  $\mu\text{m}$  thick copper layer.

Then the surface is electrolytically treated in a conventional copper-electrolyte with the result that a 20  $\mu\text{m}$  thick copper layer is formed atop the chemical copper layer.

5

Finally, the surface is electrolytically treated in a commercial silver electrolyte (Engbright A silver bath, Engelhard Corporation, Iselin, NJ, USA) with the result that a 5  $\mu\text{m}$  thick silver layer is formed atop the electrolytic copper layer.

After drying of the article at 130°C, the adhesion of the plated layers was examined  
10 by means of the scribe-grid test according to ASTM D 3002 or DIN EN ISO 2409.

By the scribe-grid test, two or more parallel lines or a rectangular pattern are cut by means of a sharp instrument. The cut is made to the substrate, and the distance between the lines should be approximately ten times the layer thickness, but at least 0.4 mm. The adhesion is too poor when the coating between the lines falls off. Samples  
15 produced according to the present example meet as a minimum ISO Class or ASTM Class 4B, which corresponds to the fact that only insignificant defects are found at the location where two scratches intersect one another. Quantitatively, these defects do not exceed 5% of the total area of the surface.

However, due to the lacking adhesion, the treated polycarbonate material cannot be  
20 plated by means of the conventional method described in the introduction to the description, where a treatment is carried out by means of permanganate followed by an etching off of the manganese dioxide and then a treatment by means of colloidal palladium due to the lacking adhesion.

The above description of the invention reveals that it is obvious that it can be varied  
25 in many ways. Such variations are not to be considered a deviation from the scope of

the invention, and all such modifications which are obvious to persons skilled in the art are also to be considered comprised by the scope of the succeeding claims.